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STUDIES ON THE REDUCTION OF SULFONIC ACIDS

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BY

BEN EDMUND SORENSON

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[Contribution from the School of Chemistry of the University of Minnesota]

REDUCTION OF ALIPHATIC SULFONIC ACID SALTS WITH PHOSPHORUS PENTABROMIDE AND PHOSPHORUS TRIBROMIDE[1]

By W. H. Hunter and B. E. Sorenson

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In an attempt to prepare tribromobenzene sulfonyl bromide from the sodium salt of the sulfonic acid and phosphorus pentabromide, it was found that the reaction took a different course from that anticipated. Instead of the expected sulfonyl bromide, hexabromodiphenyl disulfide[2] was obtained. Further investigation showed that this reaction was quite general for salts of aromatic sulfonic acids.

The present work is an extension of this investigation to include the salts of the aliphatic sulfonic acids.

The sodium or potassium salts of methyl-, ethyl-, butyl-, isoamyl and benzylsulfonic acids, and the potassium salt of β-sulfo-β-phenylpropionic acid were prepared and treated with phosphorus bromides. In general this was carried out as follows: one mole of the salt was treated with one mole of phosphorus pentabromide (to form the sulfonyl bromide) and the reaction mixture was then further treated with two and one-half moles of phosphorus tribromide to bring about the reduction. In some cases this procedure was varied by allowing phosphorus pentabromide alone to react upon the sulfonate, and in one case the sulfonyl bromide was isolated and treated with phosphorus tribromide.

All the salts mentioned gave the corresponding disulfides when treated with *mixed* phosphorus bromides, except β-potassium sulfo-β-phenylpropionic acid, which gave β-bromo-β-phenylpropionic acid by the replacement of the SO_3K group by bromine as represented in the equations

$$C_6H_5CH(SO_3K)CH_2COOH + 2PBr_5 \longrightarrow C_6H_5CH(SO_2Br)CH_2COBr + 2POBr_3 + KBr + HBr$$

$$C_6H_5CH(SO_2Br)CH_2COBr + PBr_5 \longrightarrow C_6H_5CHBrCH_2COBr + SOBr_2 + POBr_3$$

This is similar to the action of phosphorus pentachloride on sulfonyl chlorides,[3] except that it takes place at a lower temperature.

When phosphorus pentabromide was used alone, in sufficient quantities to cause reduction to occur, according to the reaction postulated in the

[1] The work described in this paper formed part of a thesis submitted to the Graduate Faculty of the University of Minnesota by B. E. Sorenson in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. Smith.

[2] Kohlhase, This Journal, **54**, 2441 (1932).

[3] Carius, *Ann.*, **114**, 142 (1860); Barbaglia and Kekulé, *Ber.*, **5**, 876 (1872).

first paper of this series,[2] the product isolated was usually the disulfide, but in some cases the sulfonyl bromide or the alkyl bromide resulted. Substitution of hydrogen by bromine also took place in several cases. Thus, β-potassium sulfo-β-phenylpropionic acid gave α,β-dibromophenylpropionic acid.

$$C_6H_5CH(SO_3K)CH_2COOH \xrightarrow{PBr_5} C_6H_5CHBrCHBrCOOH$$

The results are summarized in Table I.

TABLE I

RESULTS OBTAINED BY REDUCING VARIOUS ALIPHATIC SULFONATES AND SULFONYL BROMIDES WITH PHOSPHORUS BROMIDES

Reactant	Reagent	Product	Yield, %
CH_3SO_3K	$PBr_5 + PBr_3$	$(CH_3)_2S_2$	26
$C_3H_5SO_3K$	$PBr_5 + PBr_3$	$(C_3H_5)_2S_2$	54
$C_2H_5SO_3K$	PBr_5	$C_2H_5SO_2Br$	41
n-$C_4H_9SO_3K$	PBr_5 (1 mole)	n-$C_4H_9SO_2Br$	66
n-$C_4H_9SO_3K$	PBr_5 (3.5 moles)	$(n$-$C_4H_9)_2S_2$	49
n-$C_4H_9SO_3K$	$PBr_5 + PBr_3$	$(n$-$C_4H_9)_2S_2$	52
n-$C_4H_9SO_2Br$	PBr_3	$(n$-$C_4H_9)_2S_2$	63
iso-$C_5H_{11}SO_3Na$	$PBr_5 + PBr_3$	$(iso$-$C_5H_{11})_2S_2$	55
$C_6H_5CH_2SO_3Na$	$PBr_5 + PBr_3$	$(C_6H_5CH_2)_2S_2$	87
$C_6H_5CH_2SO_3Na$	PBr_5	$C_6H_5CH_2Br$	70
$C_6H_5CH(CO_2K)CH_2COOH$	$PBr_5 + PBr_3$	$C_6H_5CHBrCH_2COOH$	80
$C_6H_5CH(SO_3K)CH_2COOH$	PBr_5	$C_6H_5CHBrCHBrCOOH$	62

Experimental Part

Potassium Alkyl Sulfonates.—These were made by oxidizing the corresponding alkyl thiocyanates with nitric acid (sp. gr. 1.42).[4] The reaction mixtures were neutralized with potassium carbonate and evaporated to dryness. The crude potassium alkyl sulfonates so obtained were purified by recrystallizing from 95% alcohol.

TABLE II

PROPERTIES OF POTASSIUM ALKYL SULFONATES

Sulfonate	Yield, %	Analyses, % Calcd. K	Calcd. S	Found K	Found K	Found S	Found S
Methyl	90						
Ethyl	80						
n-Butyl	70	22.19	18.21	22.05	22.06	18.55	18.42
Isoamyl[a]	41	13.22 (Na)	18.41	13.19	13.10	18.78	18.90

[a] The sodium salt was made by oxidizing 50 g. of isoamyl disulfide with 20 cc. of nitric acid (sp. gr. 1.42).

Alkyl Sulfonyl Bromides.—One-tenth mole of potassium alkyl sulfonate and 0.35 mole of phosphorus pentabromide were heated for forty minutes at 70–80°, poured into 400 g. of crushed ice and stirred continuously until about 60 cc. of clear liquid remained undissolved. The lower layer was separated and shaken in a separatory funnel with 200 g. of ice for two minutes. The lower layer was separated, dried with calcium chloride and fractionated.

[4] Muspratt, *Ann.*, **65**, 261 (1848).

TABLE III

PROPERTIES OF ALKYL SULFONYL BROMIDES

Sulfonyl bromide	Yield, %	Boiling point, °C.	d_4^{25}	Analyses, % Calcd. S	Calcd. Br	Found, S	Found, Br	M. p. of sulfonamide, °C.
Ethyl[a]	41	103–106 (40 mm.)[b]		18.50		20.44 20.30		57–58
n-Butyl	66	101–102 (11 mm.)	1.5109	15.94	39.75	15.58 15.51	40.03 39.93	

[a] *J. prakt. Chem.*, [2] **26**, 384 (1880).

[b] Cherbuliez and Schnauder [*Helv. Chim. Acta*, **6**, 249 (1923)] give 80° (13 mm.).

Alkyl Disulfides.—One-third mole of finely ground potassium alkyl sulfonate was mixed with 0.33 mole of phosphorus pentabromide, after which the reaction flask was fitted with a calcium chloride tube and heated on a steam-bath for fifteen minutes. After cooling to 80°, 0.8 mole of phosphorus tribromide was added and the temperature maintained at 70–80° for forty minutes. The red reaction mixture was transferred to a 1-liter flask, cooled in an ice-bath and dissolved in 250 cc. of ether. The halides of phosphorus were hydrolyzed by adding water slowly until the ether formed a separate layer, and then the solution was steam distilled. The ether layer of the distillate was separated, washed once with water, then with 5% sodium carbonate solution and finally with water. After drying with calcium chloride, it was filtered and fractionated, using a Clarke flask with column attached.

TABLE IV

PROPERTIES OF ALKYL DISULFIDES

Disulfide	Yield, %	Boiling point, °C.	$d_4^{X°}$	Analyses Sulfur Calcd.	Sulfur Found		$AgNO_3$ double salt Ag, calcd.	$AgNO_3$ double salt Ag, found	
Methyl	26	108–108.5 (748 mm.)[a]	1.0606 (16°)	68.08	68.54	68.43	40.87	40.69	40.84
Ethyl	54	151–152 (736 mm.)[b]	0.9961 (20°)[b]	52.47	52.96	52.89	38.95	37.01	36.88
n-Butyl[c]	52	227–229 (735 mm.)	.9327 (25°)	35.95	36.63	36.57			
Isoamyl	55	123.5–124 (12 mm.)	.9188 (18°)[d]	31.08	31.73	31.68			
Benzyl	87	(m. p. 70–71.5°)[e]		26.06	26.87	26.75			

[a] Pierre [*Ann.*, **80**, 128 (1830)] gives 112.1 (744 mm.). [b] Wasini [*Ber.*, **15**, 2882 (1882)] gives b. p. 152.8–153.4° (corr.); d_4^{20} 0.9927. [c] Phosphorus pentabromide alone gave 49%, b. p. 224–233°. Phosphorus tribromide alone gave 63%. [d] Henry [*Jahresb.*, **48**, 699 (1847)] gives d_4^{18} 0.918. [e] Hofmann [*Ber.*, **20**, 15 (1887)] gives 71–72°.

Preparation of *n*-Butyl Disulfide by a Known Method.—Since *n*-butyl disulfide was not described in the literature, it was made by refluxing an alcoholic solution of sodium disulfide with *n*-butyl chloride. The alcohol and excess butyl chloride were distilled off at atmospheric pressure and enough water added to dissolve the sodium chloride. The oily upper layer was separated, dried and fractionated at reduced pressure. *n*-Butyl disulfide was water white and had the following properties: b. p. 93–94° (7 mm.) or 226–229° (740 mm.), d_4^{25} 0.9329.

Anal. Calcd. for $C_8H_{18}S_2$: S, 35.95. Found: S, 36.64, 36.50.

n-Butyl trisulfide, the by-product, was pale yellow and had the following properties: b. p. 119–121° (6 mm.) and d_4^{25} 1.0117.

Anal. Calcd. for $C_8H_{18}S_3$: S, 45.73. Found: S, 46.50, 46.62.

Preparation of Benzyl Bromide from Sodium Benzyl Sulfonate.—Benzyl bromide was obtained in 70% yield when fifteen grams of sodium benzyl sulfonate and 93 g. of phosphorus pentabromide were heated at 85–90° for fifteen minutes. The mixture,

which fused and gave off hydrogen bromide, was dissolved in 100 cc. of ether, and water was added until the ether layer separated. The ether solution was separated, washed once with water and dried with calcium chloride. After evaporating the ether, the residual liquid was fractionated at 18 mm., and redistilled at atmospheric pressure; b. p. 195–197° (740 mm.).

Anal. Calcd. for C_7H_7Br: Br, 46.73. Found: Br, 48.64, 48.33.

Preparation of β-Bromo-β-phenylpropionic Acid.—Eighteen grams of β-potassium sulfo-β-phenylpropionic acid (made from cinnamic acid and potassium sulfite by the method of Valet [*Ann.*, **154**, 63 (1870)] and purified by washing with benzene and recrystallizing from alcohol), 58 g. of phosphorus pentabromide and 45 g. of phosphorus tribromide were heated at 85–90° with occasional shaking until the phosphorus pentabromide was dissolved. The reaction mixture was cooled and dissolved in 125 cc. of ether. The ether solution was treated with water to hydrolyze the phosphorus bromides, dried, filtered and evaporated to dryness. This gave 12 g. (80%) of crude gray β-bromo-β-phenylpropionic acid, which was crystallized twice from benzene to give a colorless material, m. p. 135–137°. An authentic sample of β-bromo-β-phenylpropionic acid melted at 137°; mixed m. p. 135.5–137°.[5]

Preparation of α,β-Dibromo-β-phenylpropionic Acid.—Nineteen grams of β-potassium sulfo-β-phenylpropionic acid and 125 g. of phosphorus pentabromide were mixed and heated at 100° until the evolution of hydrogen bromide ceased (about one hour). The reaction product was isolated in the same way as the β-bromo-β-phenylpropionic acid. The crude product was crystallized once from benzene, giving 13.2 g. (62%) of α,β-dibromo-β-phenylpropionic acid, m. p. 188–195° (with decomposition). It was recrystallized and melted at 197° (when heated rapidly near the melting point).[6]

Anal. Calcd. for $C_9H_8O_2Br_2$: Br, 51.94. Found: Br, 51.60, 51.80.

Summary

1. Several salts of aliphatic sulfonic acids were reduced to the corresponding disulfides with a mixture of phosphorus pentabromide and phosphorus tribromide.

2. Phosphorus pentabromide alone gave the same disulfides in some cases. In other cases the sulfonic acid group was replaced by bromine.

3. The sulfonyl bromide group is more easily replaced by bromine (by means of phosphorus pentabromide) when attached to an aliphatic radical than when attached to an aromatic nucleus.

4. The presence of a phenyl radical on the carbon holding the sulfonyl bromide group facilitates the replacement of the latter by bromine.

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[5] Bodwig, *Ber.*, **12**, 538 (1874).

[6] Sudborough and Thompson [*J. Chem. Soc.*, **83**, 670 (1903)] give the melting point as 197° (when heated rapidly).

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[Contribution from the School of Chemistry of the University of Minnesota]

THE MECHANISM OF THE REDUCTION OF SULFONYL BROMIDES WITH PHOSPHORUS TRIBROMIDE[1]

By W. H. Hunter and B. E. Sorenson

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Kohlhase[2] discovered that many aromatic sulfonyl bromides could be easily and conveniently reduced to disulfides by phosphorus tribromide. Hunter and Sorenson[3] showed that the reaction could be applied with equal success to sulfonyl bromides of the aliphatic series. These earlier papers were concerned largely with the preparative aspects of the new reaction. Attention was logically next devoted to the mechanism of the change.

In order to elucidate the mechanism of the reaction, two methods of attack are possible: attempts could be made to isolate intermediate products of the reduction, or possible intermediate products could be synthesized by other means, and the action of phosphorus bromides upon these substances studied. Since the first procedure is attended with great difficulty and uncertainty under the conditions necessary for these reductions, we chose the latter method of attack.

For this purpose it was first assumed that the reaction took place in steps which might be represented as

$$RSO_2Br + PBr_3 \longrightarrow RSOBr + POBr_3 \quad (1)$$
$$RSOBr + PBr_3 \longrightarrow RSBr + POBr_3 \quad (2)$$
$$2RSBr + PBr_3 \longrightarrow RSSR + PBr_5 \quad (3)$$

Examples of each of these possible intermediate products were prepared and subjected to the action of phosphorus tribromide as described in this paper.

No sulfinyl bromides were described in the literature; therefore, *p*-toluene sulfinyl chloride[4] was chosen for the first experiments. This sulfinyl chloride was reduced very readily by phosphorus tribromide, although it gave a slightly lower yield of *p*-toluene disulfide than *p*-toluene sulfonyl bromide which was also reduced as a control.[5]

[1] This article is an abstract of part of a thesis submitted by B. E. Sorenson to the Faculty of the Graduate School of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in June, 1927. The manuscript was written by the junior author after the death of Dr. Hunter.—L. I. Smith.

[2] Kohlhase, This Journal, **54**, 2141 (1932).

[3] Hunter and Sorenson, *ibid.*, **54**, 3364 (1932).

[4] Hilditch and Smiles, *Ber.*, **41**, 4115 (1908).

[5] The comparison between the *p*-toluene sulfinyl chloride and the sulfonyl bromide was not entirely logical, but since previous work[2] has shown that sulfonyl chlorides are not reduced by phosphorus tribromide whereas sulfonyl bromides are readily reduced, it seems probable that the sulfinyl bromide would be reduced at least as easily as the sulfinyl chloride.

Otto and Rössing[6] also found that sodium benzene sulfinate was reduced to the disulfide by phosphorus trichloride according to the equation

$$6C_6H_5SO_2Na + 9PCl_3 \longrightarrow 3(C_6H_5S)_2 + 3NaCl + 8POCl_3 + Na_3PO_4$$

If the first product of this reaction is the sulfinyl chloride it indicates that this is reduced by the phosphorus trichloride. Since sulfonyl bromides are not reduced by phosphorus trichloride,[2] this can be adduced as further evidence that sulfinyl bromides are more easily reduced than sulfonyl chlorides. This ease of reduction of the sulfinyl bromides very likely accounts for the fact that sulfinyl bromides do not appear as intermediate products.

o-Nitrophenyl sulfur bromide[7] was chosen for the next experiments as it was well known and quite stable. This sulfur bromide did not react rapidly with phosphorus tribromide. However, when it was allowed to stand for several days in dry ether with phosphorus tribromide it gave some *o*-nitrophenyl disulfide. Under similar conditions the sulfur bromide alone in dry ether also gave some *o*-nitrophenyl disulfide but not as much as when phosphorus tribromide was present. These phenomena may be explained by assuming that the sulfur bromide dissociates reversibly into bromine and the disulfide, and that phosphorus tribromide may upset the equilibrium by combining with the bromine thus liberated.

$$2RSBr \rightleftharpoons RSSR + Br_2$$
$$Br_2 + PBr_3 \rightleftharpoons PBr_5$$

When *o*-nitrophenyl disulfide was treated with an excess of phosphorus pentabromide, *o*-nitrophenyl sulfur bromide was formed, thus proving that the above reaction is in fact reversible. An attempt was made to prepare tribromobenzene sulfur bromide from the disulfide and bromine according to the general method of Zincke and Farr[7] but it could not be isolated. As soon as the solvent and excess bromine were removed the reaction was completely reversed to give back the disulfide.

o-Nitrophenylsulfonyl bromide was reduced by phosphorus tribromide at low temperatures. The products were the disulfide and the sulfur bromide when the reaction products were isolated in the absence of water. When the reaction mixture was dissolved in ether and hydrolyzed by adding water, *o*-nitrophenyl disulfide and *o*-nitrothiophenol were obtained.

Thionaphthol[2] was previously isolated in this type of reduction and was assumed to be formed in accordance with the equations

$$RSSR + PBr_3 \rightleftharpoons (RS)_2 \cdot PBr_3$$
$$RSSR \cdot PBr_3 + 4H_2O \longrightarrow 2RSH + 3HBr + H_3PO_4$$

This mechanism was tested by mixing *o*-nitrophenyl disulfide and phosphorus tribromide, but no thiophenol resulted. The next postulate was

[6] Otto and Rössing, *Ber.*, **24**, 3883 (1891).

[7] Zincke and Farr, *Ann.*, **391**, 67 (1912).

that the thiophenol resulted from the further reduction of the sulfur bromide when water was added to the ether solution. However, none of the reducing agents present in the reaction mixture, such as phosphorus acid and hydrobromic acid, reduced the sulfur bromide to the thiophenol in the presence of water and ether. However, pure *o*-nitrophenyl sulfur bromide and phosphorus tribromide in ether solution gave almost a quantitative yield of thiophenol when water was added. From this it was concluded that the thiophenol resulted from the hydrolysis of a molecular compound first formed from the sulfur bromide and phosphorus tribromide.

$$RSBr + PBr_3 \rightleftharpoons RSPBr_4 \xrightarrow{H_2O} RSH + POBr_3 + HBr$$

A freezing point method was devised to determine if evidence of the formation of a molecular compound could be obtained. Phosphorus tribromide or *o*-nitrophenyl sulfur bromide alone gave normal freezing point depressions in benzene. Likewise, the mixture gave a normal freezing point depression in benzene showing that no molecular compound was formed in this solvent. However, when a solution of the two in *benzene* was hydrolyzed (as was done with the ether solution) *o*-nitrophenyl disulfide was formed instead of the thiophenol obtained in ether. No direct proof of the presence of a molecular compound in the ether solution could be observed, but the different results obtained in ether and in benzene strengthened our opinion that some such explanation was probably correct.

On the basis of all the evidence we are able to postulate definitely that the steps in the reduction of sulfonyl bromides to disulfides are the following:

$$RSO_2Br + PBr_3 \longrightarrow RSOBr + POBr_3 \quad (1)$$

$$RSOBr + PBr_3 \longrightarrow RSBr + POBr_3 \quad (2)$$

$$2RSBr \rightleftharpoons RSSR + Br_2 \quad (3)$$

$$Br_2 + PBr_3 \rightleftharpoons PBr_5 \quad (4)$$

$$RSBr + PBr_3 \overset{\text{ether}}{\rightleftharpoons} RSPBr_4 \quad (5)$$

$$RSPBr_4 + 4H_2O \longrightarrow 2RSH + 2H_3PO_4 + 4HBr \quad (6)$$

Experimental

Preparation of *p*-Toluenesulfinyl Chloride.—*p*-Toluenesulfinyl chloride was made by treating *p*-toluenesulfinic acid with an excess of thionyl chloride according to the method of Hilditch and Smiles.[8] The material obtained was a liquid at room temperature. The above authors give the melting point as 54–58°.

Reaction between *p*-Toluenesulfinyl Chloride and Phosphorus Tribromide.—(a) Four grams (1 mole) of *p*-toluenesulfinyl chloride and 10 g. (1.5 moles) of phosphorus tribromide were mixed in a 50-cc. flask. The mixture became so hot that free bromine was given off and phosphorus pentabromide sublimed on the neck of the flask. When the reaction mixture became cool it was dissolved in 30 cc. of ether and water was added to hydrolyze the halides of phosphorus. The ether layer was separated, washed with sodium carbonate solution and dried. The ether was evaporated and the residual red oil allowed to solidify. This gave 1.5 g. (54% of the theoretical quantity) of crude *p*-

[8] Ref. 4, p. 4114.

toluene disulfide. This was crystallized from alcohol and gave a colorless product of m. p. 44–45°. *p*-Toluene disulfide melts at 46°.[9]

Anal. Subs., 0.1190: $BaSO_4$ (Carius) 0.2308. Calcd. for $C_{14}H_{14}S_2$: S, 26.06. Found: S, 26.62.

Reaction between *p*-Toluenesulfonyl Bromide and Phosphorus Tribromide.—Three grams (1 mole) of *p*-toluenesulfonyl bromide[10] was heated with 8.7 g. (2.5 moles) of phosphorus tribromide at 80–90° for twenty minutes. The *p*-toluene disulfide was isolated as in the previous experiment, and weighed 0.9 g. (56% of the theoretical). The recrystallized disulfide melted at 44–45°, and showed no depression when mixed with a sample prepared as in the previous experiment.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether.—One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 20 cc. of dry ether. To this 2.8 g. of phosphorus tribromide was added. The flask was stoppered and allowed to stand for five days. After several hours the solution became cloudy and in about eight hours a precipitate began to separate. This was filtered off after twenty-four hours and washed with benzene to remove a small amount of a green amorphous material. The disulfide weighed 0.05 g. (15%), m. p. 193–194°; mixed melting point with known *o*-nitrophenyl disulfide, 193–194.5°. The known disulfide melted at 195°. In a check experiment a yield of 5% of the disulfide was obtained.

The Action of Phosphorus Pentabromide on *o*-Nitrophenyl Disulfide in Dry Ether.—In a flask were placed 2 g. (1 mole) of *o*-nitrophenyl disulfide, 7 g. (3 moles) of phosphorus pentabromide and 50 cc. of dry ether. The *o*-nitrophenyl disulfide dissolved completely after about two hours. The ether solution was decanted from a small amount of a heavy red oil and evaporated at reduced pressure until a precipitate started to form. It was then treated with 50 cc. of ligroin and stirred until the precipitate was pale yellow. The solution was filtered and the precipitate washed several times with petroleum ether and dried. There resulted 1.2 g. (40%) of *o*-nitrophenyl sulfur bromide. The product melted at 78–81° after crystallization from benzine. Mixed with known *o*-nitrophenyl sulfur bromide it melted at 78–83°. The known product melted at 83–84°.

Attempt to Prepare Tribromophenyl Sulfur Bromide from Hexabromodiphenyl Disulfide and Bromine.—2.7 g. of hexabromodiphenyl disulfide was suspended in a mixture of 20 cc. of carbon tetrachloride and 4 cc. of bromine. The disulfide dissolved slowly and after twelve hours was all in solution. The carbon tetrachloride was evaporated in a vacuum desiccator. The solid which remained melted at 215–217°. The original disulfide melted at 215–217°; mixed m. p. 215–217°.

Preparation of *o*-Nitrophenylsulfonyl Bromide.—This compound was prepared by a modification of the process of Zincke and Farr[7] for the preparation of sulfonyl chlorides.

Fifteen grams of *o*-nitrophenyl disulfide was suspended in 100 cc. of glacial acetic acid. To this was added 20 cc. of bromine dissolved in 100 cc. of glacial acetic acid. The mixture was heated at 50–60° until the disulfide dissolved. Water was added slowly until the total volume of the solution was about 500 cc. If the first addition of water caused a yellow bulky precipitate to form, it was necessary to heat the reaction mixture until this redissolved. The crude sulfonyl bromide which separated as a pink or colorless precipitate was filtered off, washed with water and dissolved in a small amount of ether without drying. The water was separated from the ether solution and after concentrating the ether to a volume of 35 cc. the sulfonyl bromide was precipitated by adding ligroin. The sulfonyl bromide was filtered off, washed once with ligroin and dried. The yield was 20 g. (79%); m. p. 62.5–63.5°. Recrystallized once from equal parts of benzene and benzine, a colorless product was obtained, m. p. 63–64° (uncorr.).

[9] *J. prakt. Chem.*, [2] **41**, 190 (1890).

[10] Otto, *Ann.*, **142**, 98 (1867).

Anal. Subs., 0.2488, 0.2215: AgBr (Carius), 0.1766, 0.1560. Calcd. for $C_6H_4O_4NBrS$: Br, 30.04. Found: Br, 30.24, 29.97.

For further identification, the sulfonyl bromide was converted to the sulfonamide by saturating a ligroin–benzine solution with dry ammonia. The amide melted at 190.5–191.5° after recrystallizing from water. *o*-Nitrophenylsulfonamide[11] melts at 190–191°.

The Action of Phosphorus Tribromide on *o*-Nitrophenylsulfonyl Bromide.—Three grams (1 mole) of *o*-nitrophenylsulfonyl bromide was placed in a 100-cc. flask fitted with a dropping funnel. The flask was cooled in an ice-bath and 7.6 g. (2.5 moles) of phosphorus tribromide was added slowly through the dropping funnel. The reaction mixture was then agitated with 20 cc. of ligroin until only a flocculent yellow precipitate and a small amount of tarry material on the bottom of the flask remained undissolved. The crude yellow *o*-nitrophenyl sulfur bromide was filtered and the tar extracted with hot benzene. The crude sulfur bromide was crystallized from benzine and gave 1.1 g., m. p. 79–82°; mixed m. p. with known *o*-nitrophenyl sulfur bromide (m. p. 83–84°) was 80–83°.

Anal. Subs., 0.1242, 0.1214: AgBr (Carius), 0.0985, 0.0963. Calcd. for $C_6H_4O_3NBrS$: Br, 34.14. Found: Br, 33.68, 33.75.

The residue which did not dissolve in the benzine in the second crystallization was extracted with the benzene used to extract the original residue in the flask. The solution was filtered and evaporated to a volume of 4 cc. The precipitate which formed on cooling was filtered, washed with dilute sodium hydroxide solution and dried. There was obtained 0.3 g. of crude *o*-nitrophenyl disulfide. It was recrystallized from benzene and melted at 192.5–193.5°. *o*-Nitrophenyl disulfide[12] melts at 195°. Mixed with known disulfide it melted at 193–194°.

If instead of isolating the reaction products as described above, the reaction mixture was dissolved in ether and hydrolyzed by adding water slowly, the products were *o*-nitrothiophenol and *o*-nitrophenyl disulfide. These were separated by extracting with normal sodium hydroxide solution. After filtration the thiophenol was reprecipitated by adding dilute hydrochloric acid. The crude disulfide was purified by recrystallizing from benzene. The *o*-nitrophenyl disulfide melted at 194–195°. The *o*-nitrothiophenol melted at 54–55°. Mixed with known *o*-nitrothiophenol (m. p. 56–56.5°) it melted at 54–55°.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Disulfide in Ether.—One gram of *o*-nitrophenyl disulfide was suspended in 15 cc. of ether. To this was added 3 cc. of phosphorus tribromide. The phosphorus tribromide was hydrolyzed by adding water slowly without cooling. When 15 cc. of water had been added the mixture was allowed to stand at room temperature until the ether evaporated. The precipitate which resulted was filtered off, washed with water and dried. This gave 0.95 g. of *o*-nitrophenyl disulfide, m. p. 194–195°. The original disulfide melted at the same temperature.

The Action of Phosphorus Tribromide on *o*-Nitrophenyl Sulfur Bromide in Ether and in Benzene.—(*a*) **In ether:** 0.5 g. of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. The solution was diluted with 10 cc. of ether; 10 cc. of water was added to the ether solution drop by drop without cooling, and the mixture was allowed to stand until the ether layer evaporated. The crystals which formed were filtered, washed with cold water and dried. This gave 0.3 g. (93%) of crude *o*-nitrothiophenol; m. p. 49–51°. It was dissolved in normal sodium hydroxide solution,

[11] Ekbom, *Ber.*, **35**, 657 (1902).

[12] Wohlfahrt, *J. prakt. Chem.*, **66**, 553 (1902).

reprecipitated with hydrochloric acid, filtered, washed with water and dried. The purified thiophenol melted at 56–56.5°. *o*-Nitrothiophenol[13] melts at 56°.

Anal. Subs. 0.1415: $BaSO_4$, 0.2070. Calcd. for $C_6H_5O_2NS$: S, 20.20. Found: S, 20.09.

(*b*) **In Benzene:** One-half gram of *o*-nitrophenyl sulfur bromide was dissolved in 2.8 g. of phosphorus tribromide. To this 10 cc. of benzene was added. The reaction mixture was hydrolyzed as in part (*a*). The crystals formed were stirred with sodium hydroxide solution, filtered, washed with water and dried. This gave 0.25 g. (92% of theoretical) of *o*-nitrophenyl disulfide; m. p. 192–194°; no depression when mixed with known *o*-nitrophenyldisulfide (m. p. 195°). The sodium hydroxide filtrate was acidified with hydrochloric acid but no *o*-nitrothiophenol separated.

Determination of Freezing Points

***o*-Nitrophenyl Sulfur Bromide in Benzene.**—Sample 0.4995; benzene 17.40; depression 0.600°. Calcd. for $C_6H_4O_2NBrS$: mol. wt. 234. Found: 239.

Phosphorus Tribromide and *o*-Nitrophenyl Sulfur Bromide in Benzene.—The experiment was carried out in the same way as molecular weight determinations by the cryoscopic method. The phosphorus tribromide was added to the benzene first and the freezing point depression noted. An equivalent weight of *o*-nitrophenyl sulfur bromide was added to this in three portions and the freezing point observed after each addition.

Substance added	Freezing point, °C.
Pure benzene	4.920
0.5920 g. phosphorus tribromide	4.306
0.1280 g. *o*-nitrophenyl sulfur bromide	4.147
0.3840 g. *o*-nitrophenyl sulfur bromide	3.835
0.5120 g. *o*-nitrophenyl sulfur bromide	3.688
Depression due to phosphorus tribromide 0.614°	
Depression due to *o*-nitrophenyl sulfur bromide 0.618°	

Calcd. mol. wt. of PBr_3: 271. Found: 277. Calcd. mol. wt. of $C_6H_4O_2NBrS$: 234. Found: 233.

Summary

1. *p*-Toluene-sulfinyl chloride was reduced readily to *p*-toluene disulfide by phosphorus tribromide.

2. *o*-Nitrophenyl sulfur bromide was slowly reduced by phosphorus tribromide to give the corresponding disulfide in poor yield. The presence of phosphorus tribromide increased the yield of disulfide.

3. Phosphorus pentabromide reacted with *o*-nitrophenyl disulfide to give *o*-nitrophenyl sulfur bromide.

4. *o*-Nitrophenyl sulfonyl bromide was reduced to *o*-nitrophenyl sulfur bromide by phosphorus tribromide.

5. The action of water on an ether solution of *o*-nitrophenyl sulfur bromide and phosphorus bromide gave *o*-nitrothiophenol.

6. It is therefore postulated that the course of the reduction of a sulfonyl bromide by phosphorus tribromide is as follows: sulfonyl bromide $\rightarrow$ sulfinyl bromide $\longrightarrow$ sulfur bromide $\rightleftarrows$ disulfide + Br_2. Sulfur

[13] Mayer, *Ber.*, **42**, 3059 (1909).

bromide + PBr_3 (in ether) ⟶ addition compound ⟶ thiophenol (on hydrolysis).

MINNEAPOLIS, MINNESOTA

VITA

Author—Ben Edmund Sorenson.

Born—Jackson, Minnesota, April 22, 1899.

Academic History—Graduated from the Jackson, Minnesota, high school. B.S. in Chemical Engineering 1923, University of Minnesota. Entered the Graduate School, University of Minnesota, October, 1923; received the M.S. degree in June, 1924; received the Ph.D. in July, 1927, major Organic Chemistry, minor Chemical Engineering.

Present Position—Research Chemist, Du Pont Company, 3500 Grays Ferry Road, Philadelphia, Pennsylvania, 1927– .